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Project No. 1158-5

December 2, 1963

Dear Norb:

Enclosed are three (3) copies of the final report entitled "X-Ray Diffraction Analysis of Micro Quantities of Chemical Substances" as requested. The objective of this program has been successful in the development of an improved x-ray diffraction procedure capable ofiidentifying small (0.001 milligram) quantities of chemicals.

The Termatrex system for the filling and retrieving of powder diffraction data is arranged for only a portion of inorganic compounds. These reference compounds are coded for d/n values only giving no consideration to the important relationship between intensities and d/n. The original ASTM index considers both and supplies other crystallographic properties.

Organic chemicals may be coded by the ASTM system or a modified Termatrex system. To do this would necessitate referencing by x-ray diffraction a voluminous number of pure organic compounds to be used later in the retrieval of data for unknown identification. Unfortunately, no such system for organic compounds is available commercially but must be developed by each organization to fulfill their specific needs.

The report has been written to include your ideas and recommendations which were discussed in conference with Bill and you.

We are asking permission to publish portions of the report. We would consider the common compounds only in the publications.

Sincerely,

George

X-RAY DIFFRACTION ANALYSIS OF MICRO QUANTITIES OF CHEMICAL SUBSTANCES

Project No. 1158-5

December 2, 1963

Prepared by:

Bill

Approved

George

George

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I. STATEMENT OF THE PROBLEM

The objective of this program was to develop and improve an x-ray diffraction procedure capable of identifying small (0.001 milligram) quantities of chemicals.

II. OBJECTIVES FOR FINAL REPORTING PERIOD

During the last reporting period the objectives of the program were the continuation of the catalogue program, especially the addition of the diffraction patterns of certain materials supplied to us as unknowns.

III. SUMMARY AND CONCLUSIONS

During the early part of this program, we demonstrated the feasibility of producing x-ray powder diffraction patterns from microgram (0.001 milligram) quantities of materials. We have studied many compounds in detail and tabulated the data evolved in the manner of the ASTM x-ray powder data file. Over 600 runs have been made with the micro diffraction equipment. At least two or three trials are required to produce a catalogue quality diffraction pattern. For some compounds, e.g., uric acid and 2-naphthoic acid, usable diffraction patterns have been obtained from less than 0.0005 milligram. Of about 75 compounds attempted, only one failed to produce d/n data (Sample SP-1110). As a check on our work, we obtained the powder diffraction pattern from germanium dioxide (hexagonal). Measurement of this diffraction pattern yielded atomic spacings in good agreement with those listed as standard by the National Bureau of Standards. Our work demonstrates that in some cases the thickness of the sample is quite critical.

A thick sample produces a blurred pattern. Under this contract at the direction of the sponsor we procured a Termatrexsystem for the filling and retrieving of powder diffraction data. Two decks of Termatrex cards similar to the ASTM Termatrex decks have been prepared. The [redacted] decks differ from the ASTM decks only in the ranges of atomic spacings covered. As of the termination of the program, we have not entered any data on these cards. We never received instructions from the sponsor as to the coding desired.

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At the sponsor's request the Termatrex ASTM file of x-ray powder diffraction data was searched using the d/n data obtained on the "SP" unknowns. As expected, the results of this search are very much inconclusive. The Termatrex file contains no data on organic compounds and no intensity data. The Termatrex system is a tool for searching the ASTM x-ray powder data file. Termatrex is merely a supplement to and not a substitute for the ASTM file.

IV. EXPERIMENTAL PROCEDURES

A. X-Ray Diffraction Technique

When x-rays impinge upon matter, a portion of the x-rays is scattered by the atoms of the substance. If the atoms are arranged in an orderly manner, that is, if the substance is crystalline, then the scattered rays from different atomis will cancel and reinforce each other in a regular pattern. In the usual diffraction experiment, the x-ray beam is collimated into a narrow pencil of rays by pinholes in lead (see Fig. 1). The collimated narrow beam then traverses the sample of crystalline material. The sample may be a single crystal, or, as pictured in Figure 1, a powder made up of

tiny crystalline granules. The scattered or diffracted x-rays strike a photographic film. If the sample is a single crystal aligned with one of the principal axes parallel to the collimated x-ray beam, then the diffraction pattern recorded by the film will be a system of spots or streaks symmetrically distributed about the point of intersection of the undeviated beam with the film. For practical reasons, the direct beam of x-rays is not allowed to strike the film. The exposure produced by the direct beam and the fluorescent x-rays from silver, bromine, and iodine atoms would be spread over a large fraction of the central portion of the film. The direct beam is stopped by a lead cup or allowed to pass cleanly through a hole punched in the film. When the sample is powdered, the random orientation of the crystalline granules produces a series of concentric rings on the photographic film. If the powder is uniform and of the proper grain size, the rings will be of uniform intensity and width. If the powder contains granules considerably larger than optimum, then there will be spots or streaks mixed in the rings. If the powder is too fine, the rings will be weak and diffuse and may disappear altogether. (For examples of powder diffraction patterns, see Figures 10-16).

The interpretation of the diffraction pattern may be accomplished with the aid of Figure 2. The small circles represent a series of atoms in planes of spacing, d. The planes make an angle θ with the incident x-rays, lines AB and DF. It has been found experimentally that the diffracted x-ray beam behaves as though the x-rays are reflected from a plane mirror, but only at certain angles.[1] That is, the angle of diffraction (reflection) equals the angle of incidence.

[1] Clark, G. L., Applied X-Rays, McGraw-Hill, New York, 1955, pp. 95-102.

Consider then, the scattered x-ray beam defined by lines BC and FH also making an angle θ with the atomic planes. Thus the diffracted ray makes an angle 2θ with the incident ray. Note that the ray DFH is longer than ABC by the amount of EFG, i.e., the point H lags behind point C by the distance EFG. The waves at points C and H, however, will be in phase and reinforce each other if EFG is an integral number, n, of x-ray wavelengths, λ, i.e.,

$$n\lambda = EFG.$$

Now $EF = FG = BF \sin\theta$, but $BF = d$, the atomic plane spacings. Thus, $n\lambda = 2d \sin\theta$. This is the Bragg law of x-ray diffraction.[1,2] The angle θ may be determined from the distance, r, of the diffraction spot or ring from the central point and D, the distance from the sample to the film (Figure 1). In powder diffraction patterns, the diameter of the rings (2r) is readily measured. Distance D is most accurately determined by mixing some material of known atomic spacing, d, with the unknown.

B. X-Ray Source

The wavelength λ is determined by the anode or target material in the x-ray tube. Copper is a widely used material for x-ray diffraction experiments. The x-radiation from a copper target is diagrammed in Figure 3.[2,3] The characteristic copper radiations, Kα and Kβ, are superimposed on a continuous background radiation. To avoid a multiplicity of

[2]Azaroff, L. V., Norelco Reporter, Vol. VI, Nos. 4-5, pp. 76-79.

[3]Handbook of Chemistry and Physics, Chemical Rubber Publishing Co., Cleveland, 1953, pp. 2399 and 2406.

spots or rings arising from all the different wavelengths present in the output of the x-ray tube, it would be desirable to limit the x-rays to the Kα wavelength. This is accomplished readily for a copper target tube by placing a thin sheet of nickel between the x-ray tube and the pinhole collimator (Figure 1). The absorption of nickel is represented by the dashed curve of Figure 3. Thus the Kβ and the shorter continuous wavelengths from copper are greatly attenuated with respect to the Kα radiation. In general, a filter of one atomic number less than the atomic number of the x-ray target material will limit the radiation to the Kα wavelength region of the target.

C. Power Supply

In this laboratory, the source of x-rays for diffraction studies is a General Electric Type CA-7 copper target tube. This tube is mounted horizontally above a spectrogoniometer circle on a G. E. Type XRD-5 table. The x-ray tube window opposite the spectrogoniometer faces a camera track. The tube is powered by the G. E. Type XRD-5 high-voltage supply. This supply provides up to 50 kilovolts peak at 50 milliamperes. The Type CA-7 tube is limited to 35 kv and 16 ma. The XRD-5 power supply provides continuous voltage adjustment and four present current adjustments

D. Camera and Collimator

A Philips Micro Camera[4] was purchased by this project. Figure 4 shows this camera in position next to the x-ray tube. This camera consists of an airtight cylindrical body (No. 8 in Figure 4), which may be evacuated or

[4]Bergmann, M. E., Norelco Reporter, Vol. VI, Nos. 4-5, pp. 96-100.

filled with hydrogen or helium when required. The front of the body is removable and secured to the rest of the body by a threaded clamping ring (No. 9 of Figure 4). The pinhole collimator (No. 2 of Figure 4) is held in a hole by the threaded retainer (No. 1 of Figure 4). Thus, collimators may be changed readily. A nickel foil filter is usually taped over the hole in the collimator retainer. Initial work was done using a collimator consisting of two lead discs with 0.35 mm holes. We have now gone to a lead glass capillary of 0.08 mm diameter. This smaller bore collimator produces diffraction patterns of greater resolution at the expense of increased exposure times. The sample support may be moved laterally to center the sample with the axis of the pinholes. The film (No. 5 of Figure 4) is held by a clip to the film support (No. 6 of Figure 4) which plugs into a socket in the camera body. A fluorescent screen backed by lead glass (No. 6 of Figure 4) which plugs into a socket in the camera body. A fluorescent screen backed by lead glass (No. 7 of Figure 4) is provided for precise alignment of the pinholes with the x-ray beam. The assembled camera is held in a holder clamped to the camera track used on diffraction apparatus made by at least three manufacturers: Phillips, General Electric and Picker. The camera may be removed from and replaced in the holder without disturbing the alignment.

The alignment of the camera with the x-ray beam is a very tedious procedure for the tiny collimators used. The collimator itself should be removed. The retaining ring should be replaced. The camera

is placed in the support on the track. The x-rays are turned on. The track and support are then adjusted to yield the greatest x-ray intensity through the camera as evidenced by the spot of light on the fluorescent screen at the rear of the camera. The camera is then removed from the support taking care not to disturb the adjustments. The largest collimator (0.35 mm) is installed in the camera. The camera is returned to its support. The intensity of the spot of light produced by the x-rays in the fluorescent screen is checked. A magnifier is very helpful to see the spot on the fluorescent screen. The camera is again removed from the support and the 0.35 mm collimator replaced with the 80 micron collimator (Marked "4"). At this point the room should be darkened to facilitate viewing the spot of light on the screen. The aiming of the camera should be checked very carefully. The camera is now ready for making diffraction patterns as outlined below. The rings of the pattern should be uniform in all directions. The orientation of the film in the camera should be marked by cutting one corner. If the resulting pattern is non-uniform in intensity, the tilt of the camera with respect to the x-ray beam can then be ascertained by inspection. The aiming of the camera should be altered as indicated. Further exposures should be made until uniformity of pattern is achieved.

E. Samples

To insert a sample, the camera is removed from the holder and opened at the locking ring. The powdered samples are packed in small washers (No. 4 of Figure 4). These washers are made of brass or lead.

They are 1/4" in diameter. The brass washers are about 1.5 mm thick and have holes ranging from 0.35 to 1.0 mm diameter. The holes are funnel shaped on one side to facilitate filling. The lead washers are about 0.07 mm thick. Holes are punched in the lead with a sharp needle. These holes have diameters of 0.1 mm or less. Such holes (0.1 mm diameter by 0.07 mm long) will hold about one microgram (0.001 milligram) of material. Samples are retained in the lead washers by membranes of ethyl cellulose too thin to yield a diffraction pattern. Powders may be packed in the brass washers without a binder or retaining film. Since the intensity of the diffracted x-rays depends on the quantity of sample, the brass washers are usually used when plenty of sample is available. The lead washers are used to hold microgram samples. Several compounds have been studied using the very small samples (about 0.001 milligram.) (These samples are listed in Table 3. Pattern No. 2 in Figure 9 is from such a sample.) After filling, the sample-holding washer is positioned in the camera with the aid of a microscope. The entire front of the camera is placed on the stage of a microscope with the sample holder up. The camera front is positioned so that the collimator is centered in the cross hairs of the microscope ocular. The filled sample washer is put in place, and the holder is moved with respect to the camera front to align the sample with the cross hairs. Thus the sample is on the axis of the pinhole collimator. The filling of the sample washer is difficult to describe. The powder must be transfered from the mortar after grinding or directly from the sample vial and packed into the

tiny hole. This packing may be accomplished with a needle, spatula, etc. Both stereo and regular microscopes are very useful here. A weak ethylene dichloride solution of ethyl cellulose is used to form a thin membrane across the hole as required (about 5% ethyl cellulose).

The thickening of the sample in a brass washer can become too great. Figure 5 shows the rather interesting comparison of two different diffraction patterns for diformylbenzidine. The actual comparison is of the densitometer scans of the films. Curve A is a portion of the scan of a pattern made from a large sample. Note the blunted appearance of the two peaks. Curve B is a portion of the scan of a pattern made from a much smaller sample. Note that the left peak is actually resolved into two peaks; while the right peak is much sharper than in Curve A. The crucial dimension of the sample is the thickness. The sample for Curve A is 0.7 mm thick. That for Curve B is only 0.1 mm thick. In other words, the sample thickness for Curve B (0.1 mm) is on the order of the size of the x-ray beam (0.08 mm dia.).

In the same vein, the diffraction patterns reproduced in Figure 6 illustrate the effect of particle size. No. 1 in the first row of Figure 6 was made with the powdered sample as received. Notice the streaks and spots. The second photograph represents the effect of grinding the sample in a small agate mortar and pestle. The rings are now fairly uniform but exhibit a granular appearance. The last picture in the first row exhibits very uniform rings as a result of continued grinding. At this stage magnesium

oxide was added and ground together with the sample. (See Second Row, No. 4 of Figure 6). The final print shows the improvement produced by still more grinding of the sample plus magnesium oxide mixture. Very uniform rings make the scanning with the microdensitometer much easier. Furthermore, the diameters of the rings can be more precisely measured when these rings are uniform.

The size and amount of grinding of a sample must be determined by trail and error. Three trials are very often required. In most cases the first trial should utilize the sample powder as is. If sufficient material is on hand, a brass washer should be used as holder. Subsequent trials may require much grinding and a very small sample held in a pinhole in a lead foil washer. However, the first trial is almost always made with a large sample without grinding.

F. Film and Exposure

The camera is carried into a darkroom for loading with a film. The size of film required is about 35 by 40 mm. We have used industrial x-ray film (Ilford Type G and Eastman Kodak Type KK) dental film (Rinn DC-1). The dental films are already cut to size. A hole is punched in the film with a punch supplied with the camera. The film is clipped to the film support with the hole in the film centered on the hole in the support. The support is plugged in place and the front secured by the clamp ring. The camera is now ready for placement in the holder next to the x-ray tube.

Exposure requires as little as 15 minutes when the 0.35 mm collimator is in place, or as long as 16 hours with the 0.08 mm collimator. Films are developed in G. E. Supermix x-ray developer for 2 - 4 minutes, rinsed briefly in plain water, and fixed for 10 minutes in G. E. Supermix x-ray fixer and hardener. Following a 10-minute wash, the films are dipped in photo detergent and dried in air at room temperature. Representative diffraction patterns are shown by Figures 10-16. Over 600 negatives have been made during the development of this method. This large number of trials has been necessary for the determination of the optimum exposure time, sample size, film type, and even for the proper alignment of the x-ray collimator. As stated before, 2 or 3 exposures are usually required to determine the optimum conditions for producing a satisfactory diffraction pattern from a new compound.

G. Measurement of Apparent Atomic Spacing

Since we usually do not know either the order, n, or the atomic spacing, d, for a diffraction ring, the diffraction rings from a particular material are simply catalogued in terms of d/n, an apparent atomic spacing. Rewriting the Bragg equation

$$\frac{d}{n} = \frac{\lambda}{2 \sin \theta}$$

But

$$\tan 2\theta = r/D$$

$$2\theta = \arctan \frac{r}{D}$$

Hence

$$\frac{d}{n} = \frac{\lambda}{2 \sin \frac{\arctan (r/D)}{2}}$$

Since the values of d/n are determined repeatedly for many diffraction patterns, it is convenient to calculate d/n for the range of r/D values possible in a particular camera. From an accurate plot, one can then find d/n very readily.

Table 1 lists the d/n values for diffraction angles (2θ) from 4° to 45°. This table is computed for the average copper Kα radiation (1.5418 Angstrom units). Thus, d/n values can be determined readily simply by measuring the diameters of the diffraction rings on the film. The sample-to-film distance (approximately 15 mm) can be determined by measurement or from the diameter of a ring produced by an internal standard included with the sample. Magnesium oxide is a good internal standard. As an internal standard MgO produces a ring of large diameter which lies outside nearly all rings produced by the organics. This MgO ring has a d/n value of 2.10, or an r/D value of 0.935. Hence, the sample-to-film distance, D, equals the radius, r, of this large MgO ring divided by 0.935. The lead washers used for microgram samples also produce a large diameter ring which may be used as an internal standard. This lead ring has a d/n value of 2.47. As an internal standard, magnesium oxide has the drawback of being less transparent to the x-rays used (Copper Kα) than the organics being studied. The absorption of x-rays is proportional to the atomic number. Since lithium has a lower atomic number than magnesium, lithium carbonate was tried as an internal standard. Unfortunately lithium carbonate produces rings which fall in the same region as the organics.

The diameters of the diffraction rings can be measured directly on the film with a ruler. However, we have found that this measurement can be accomplished more precisely by using a magnified image of the rings. In one method the diameters of the rings are measured on the densitometer tracings (see following section). These traces present a magnified image of the spacing of the rings along a diameter, and indicate the relative densities of the rings as well. As an alternative the ring spacings are measured on a projection comparator. The film is clamped between glass plates on a carriage driven by a graduated lead screw. A magnified image of the film is projected on a screen. The lead screw is turned by hand until the ring falls on a fiducial mark on the screen. The position of the carriage can be read to 0.01 mm. Two operators were able independently to make measurements of diffraction ring diameters which were in agreement to within 1/2%. A short lead screw at right angles to the measuring screw enables the diffraction pattern to be set precisely so that the measurements of diameters are made along a diameter. (The d/n values for various compounds are tabulated in Table 5).

H. Intensity Measurement

Several factors determine the relative intensity of the diffraction rings. Among these are the atomic number of the atoms involved, the population of the planes producing the ring, and the number of possible orientations of the crystal producing the same planar spacing. Furthermore, other considerations being equal, the larger the diameter of a ring, the lower

the intensity, since the same quantity of x-rays is made to cover a larger area. The intensity of the diffraction rings is determined with a densitometer.

Figure 7 is a schematic diagram of the densitometer. Light from the concentrated filament lamp is collected by the condensing lens. The lower microscope objective focuses the region of the condensing lens onto the film emulsion. The glass jaw slit serves to limit the size of the scanning spot while still providing background illumination for focusing the system. The diffraction rings are usually so broad and diffuse compared to the sharp, narrow line produced by the glass slit, that no benefit comes from using this slit with the powder diffraction patterns. Usually, it is removed for scanning powder patterns. The upper microscope objective focuses the film emulsion on a metal jaw slit before the photo tube. The film is clamped between glass plates to hold it flat and in focus over the entire length of scan. The amount of light reaching the photo tube is reduced by the density or blackening of the particular area of the emulsion interposed between the light source and phototube. The microscope objectives reduce the size of the area scanned to microscopic proportions. Indeed, if the slit is set fine enough, individual clumps or granules of the emulsion are recognized in the output of the phototube. Usually the slit is set wide enough that the granularity of the emulsion does not contribute to the signal. Thus the phototube current is reduced in proportion to the blackening of the various rings. The blackening is taken as a measure of the intensity of a diffraction ring. The phototube output is recorded on a continuous chart, pen and ink recorder. The diffraction pattern is moved by a lead screw driven by a synchronous motor.

The chart paper moves at a much faster rate. Thus, the diameters of the various rings are magnified by ratio of chart travel to film travel per unit time.

Figure 8 is a tracing of the densitometer scan of the diffraction pattern from uric acid. (The uric acid pattern is No. 24 of Figure 11). The dark ring of the diffraction pattern produces the peaks at about 7 mm from the center of the scan. A hole is punched in the middle of the film to allow the direct beam of x-rays to bypass the emulsion, preventing blotting out of the central portion of the diffraction pattern. This hole is responsible for the two sharp peaks at the center of the densitometer scan. This pattern does not have a MgO ring. The MgO ring lies outside the scanned area presented here. (Relative intensities as determined by the densitometer are listed in Table 5, along with the apparent atomic spacings).

I. Termatrex System for Filing and Retrieving Data

The Termatrex system utilizes a square array of 10,000 hole positions in a deck of thin plastic cards. The hole positions are assigned to the items to be described, e.g., chemical compounds. Each card represents one particular characteristic that several items have in common, e.g., molecular weight. Hence, the hole positions for all compounds of one molecular weight would be drilled out. Similarly, cards may be drilled for other characteristics such as melting point, color, etc. One deck of cards is required for every 10,000 items to be described. The deck will consist of as many cards as are necessary to break down the data. The operation of the system can best be explained in terms of an actual set of cards, the

Termatrex decks for searching the ASTM x-ray powder data. There are about 150 cards divided into three decks. Deck A consists of 50 cards covering the d/n values from 1.5 to 10.0 A.U. The range of d/n values on one card varies from about 0.1 A.U. for the low end to 1.5 A.U. at the upper end. Deck B consists of 47 cards covering the same d/n values, but the ranges in Deck B are displaced about one-half range with respect to Deck A. Deck C consists of 52 cards covering the chemical elements. Major elements such as aluminum, iron, oxygen, etc., are represented by individual cards. Less frequently occurring elements, such as the rare earths, radioactive elements, noble metals, etc., are grouped together on cards. There are also cards listing the minerals, hydrates, and alloys. Oxygen and hydrogen are punched into colored transparent cards as well as opaque cards.

To use the system, one selects from either Deck A or Deck B the cards which cover the d/n values obtained from the x-ray powder diffraction pattern of an unknown substance. The selected cards are then stacked together on top of an illuminated viewing box. The cards must be in precise register with the viewing box and with each other. Where a hole position is drilled out in all cards on the viewer, light will, of course, come through. If no holes light up, then the card or cards covering the weakest diffracting ring or rings can be removed. If too many holes are lighted, then pairs of cards should be selected from both Decks A and B so that each pair covers a narrower range of d/n values. The viewing box is equipped with a coordinate system for indexing the 10,000 positions. The

"y" is read first and the "x" second, both as two digits; e.g., 0000 would be the upper left starting position. Termatrex has been set up so that the y axis is always read first. There is an index supplied with the decks which lists the Termatrex coordinates, substance, and ASTM file number. There are 5700 entries. Thus, the holes in the Termatrex cards suggest ASTM file data which may be the same substance as the unknown. If the chemical elements in the unknown have been identified, then appropriate cards from Deck C may be added to the stack on the viewer.

It must be kept in mind that the Termatrex cards only supplement the ASTM file cards. One must return to the ASTM file to get any real data on the substances covered by the Termatrex cards. The Termatrex file does not contain data on organics and does not yield intensities for the inorganic compounds listed.

J. Termatrex System for [redacted] Data 50X1

The Termatrex viewing box purchased on this program is equipped to drill the Termatrex cards as well as search them. The Termatrex people suggested that we utilize the same cards as are used for the ASTM data. Hence, we acquired blank decks A, B, and C, as described above. These decks are very obviously custom marked for the ASTM data. Our values tend to be higher than those in the ASTM file (1.5 - 10.0). We have few values less than 2.5 and we have many values between 5 and 6 where the ASTM data "thin out." Thus it was decided that our file should cover the range from 2.5 to 12.0 rather than from 1.5 to 10.0 as for the ASTM data. Table 2 lists the Termatrex card numbers and the corresponding d/n ranges. There are no

cards contemplated currently for the chemical elements, since most of our data concern organics.

As an example of the method of drilling the Termatrex cards, consider anthracene, the first entry in Table 5. Note that for anthracene we have obtained one intense ring, and six rings of intensity considerably less than the first ring. The data for the two weakest rings are dropped, leaving five rings. In general, only five or six rings from one pattern are of sufficient intensity to be considered. Indeed, the original ASTM file card sets contain only three cards for each compound. The three strongest d/n values are used to index the three cards. One card is printed for each of the three strongest values. Using the Termatrex cards, we may select as many d/n values for one compound as are really useful. For anthracene, the following cards would all be drilled at the same coordinate: from Deck A of Table 2, green/57, orange/90, green/90, green/15, and black/40; from Deck B of Table 2, green/50, orange/95, green/80, green/10, and black/44. None of the blank Termatrex cards have been drilled. We have never received definite instructions as to the Termatrex coordinates to be utilized. We were never notified whether the Termatrex coordinates for the compounds we have catalogued were to originate with us or from the outside.

V. DATA

Table 3 lists several compounds from which usable diffraction patterns were obtained from microgram (0.001 milligram) quantities of sample. For all but the last material listed sufficient sample was used to permit grinding

the samples. The microgram sample was then prepared from the ground material. The last sample was taken as received. A print of the diffraction pattern from this sample is given as No. 18 in Figure 11.

Table 4 compares data obtained at [redacted] with that published by the Bureau of Standards on the compound germanium dioxide (hexagonal). Table 5 catalogues the data obtained on about 75 materials during the course of the program. The data in the table are tabulated for each entry by the system used by the ASTM. The apparent atomic spacings (d/n) are listed in order of decreasing intensity. The data in Table 5 have been revised in many cases. Some compounds have been re-run several times to obtain good patterns.. Extraneous values due to magnesium oxide or the washer material have been weeded out. In general the data in the second half of the table exhibit more diffraction rings than those at the beginning. The later data reflect improvements in sensitivity and resolution. Figures 10-16 are contact prints of diffraction patterns.

50X1

VI. ANALYSIS OF DATA

Table 4 compares our data for a particular compound with the data published as standard by the National Bureau of Standards. The NBS data are obtained by a diffractometer and radiation counter from rather large samples. Our data are obtained photographically using very small samples. The compound chosen was germanium dioxide (hexagonal). This compound was selected since it has no state of hydration and crystallizes in only two systems, hexagonal and tetragonal. The tetragonal converts to the more

how much?

common hexagonal form upon heating. Note that our data agree within 1% with the NBS data except for our 4.27 and 1.99 values. The 4.27 ring is rather small in diameter. The larger d/n values are actually measured less precisely than the small d/n values. For the 1.99 value, the NBS data list a very weak intensity. The general agreement of the two sets of data demonstrate that our "postage stamp" films present valid x-ray powder diffraction patterns.

The most striking feature of the diffraction patterns printed in Figures 10-16 is that no two are alike. At first glance, Nos. 14, 15, and 16 in Figure 11 appear the same. However, in the printing process some detail is lost. These three patterns are made from different kinds of paper. In Table 5 the differences are quite apparent. The cellulose rings are present in each case plus other rings probably due to fillers or residues from the manufacturing process. Even the pattern from dialysis tubing, No. 17, contains most of the cellulose rings.

In Figure 12, patterns Nos. 31, 32, and 33 appear the same. Again the data in Table 5 give significant differences among these patterns. Two large rings are entirely absent in the reproduction of No. 32. Pattern No. 47 in Figure 13 comes close to reproducing most of the rings present in the negative. At least 15 rings may be counted on the negative, and most of these are reproduced here.

Most of the negatives selected for reproduction were made from sizable quantities of sample, i.e., about one-tenth milligram. However, No. 18 in

Figure 11 is a print of a diffraction pattern made using a sample of the order of 0.003 milligram. There was very little of this material available to us. Note the streaks and spots. These are due to non-uniformity in the granule size. We have no satisfactory method of grinding such a small sample to uniform grain size. Where ground material is available, we have succeeded in obtaining recognizable diffraction patterns from less than 0.001 milligram. Indeed, 0.0001 milligram of ground uric acid produced a recognizable pattern. (See Figure 9). Table 4 lists several compounds which produced usable patterns from microgram samples.

For the compounds anthracene, 8-hydroxyquinoline, and uric acid two sets of data werecobtained from fresh samples. Only the second set of data are tabulated in Table 5. The d/n values for these repeated samples agreed within 1%. At the sponsor's request the Termatrex ASTM file of x-ray powder diffraction patterns was searched using the d/n data on the "SP" unknowns in Table 5. The results of this search are given in Table 6. There are two very serious drawbacks to this procedure: first, the data in the Termatrex file are entirely from inorganic substances, and, second, the file contains no intensity data. That is, with only the Termatrex ASTM x-ray powder diffraction file available, one cannot search for organic compounds, nor can one compare intensity distributions for inorganics. However, the Termatrex data would be useful, if an elemental analysis were available for each unknown. Elemental analysis would eliminate many of the compounds listed in Table 6. If the unknowns submitted to us as organics are

contaminated with inorganic materials, then some of the compounds listed in Table 6 may quite possibly be present. Indeed, for No. SP-1115 which was labeled as a clay the Termatrex search uncovered a magnesium aluminum silicate. The Termatrex ASTM file contains many clays, talcs, and other minerals. Many substances are entered repeatedly with obviously different sets of d/n values. Many are entered under the name "Montmorillonite" with no clue as to the particular composition for which the diffraction data were obtained. As stated before, there are no intensities listed in the Termatrex file. Thus no real comparison can be made between the data obtained at [redacted] and the data in the Termatrex file. It must be pointed out 50X1 that the original ASTM powder data file contains a great deal more information for each entry than just d/n ratios. These data include intensity measurements for the d/n ratios plus physical and chemical characteristics. The present Termatrex system provides only for the d/n values.

For whatever they are worth, the results of searching the Termatrex ASTM x-ray powder diffraction file are simply listed in Table 6. There appear many compounds which are very obviously out of place here. Clays and minerals appear quite often. We cannot ascertain whether the incidence of clays is high due to the nature of the unknowns or due to the large number of such minerals entered in the ASTM file.

TABLE 1. APPARENT ATOMIC SPACING*

r/D	d/n	r/D	d/n
0.075	20.612	0.310	5.148
0.080	19.321	0.320	4.999
0.085	18.194	0.330	4.858
0.090	17.181	0.340	4.726
0.095	16.284	0.350	4.601
0.100	15.477	0.360	4.485
0.105	14.746	0.370	4.374
0.110	14.080	0.380	4.269
0.115	13.475	0.390	4.170
0.120	12.915	0.400	4.077
0.125	12.352	0.420	3.904
0.130	11.935	0.440	3.746
0.135	11.502	0.460	3.604
0.140	11.092	0.480	3.474
0.145	10.716	0.500	3.356
0.150	10.366	0.520	3.246
0.155	10.036	0.540	3.146
0.160	9.729	0.560	3.054
0.165	9.438	0.580	2.968
0.170	9.168	0.600	2.888
0.175	8.910	0.620	2.814
0.180	8.670	0.640	2.745
0.185	8.441	0.660	2.681
0.190	8.225	0.680	2.620
0.195	8.007	0.700	2.564
0.200	7.823	0.720	2.511
0.210	7.462	0.740	2.462
0.220	7.134	0.760	2.415
0.230	6.834	0.780	2.371
0.240	6.562	0.800	2.329
0.250	6.309	0.850	2.234
0.260	6.078	0.900	2.152
0.270	5.863	0.950	2.079
0.280	5.666	1.000	2.014
0.290	5.481		
0.300	5.308		

*Apparent atomic spacing (d/n) for values of the tangent (r/D) of the diffraction angle (2θ) from 4° to 45°. Radiation: Copper Kα - 1.5418 Angstrom units.

TABLE 2. d/n RANGES FOR TERMATREX CARDS
CONTAINING [redacted] POWDER DATA 50X1

DECK A

Card No.	d/n Range	Card No.	d/n Range
Yellow/22	Less than 2,500	Green/25	4.200 - 4.299
" 53	2.500 - 2.569	" 35	4.300 - 4.399
" 58	2.570 - 2.639	" 45	4.400 - 4.499
" 66	2.640 - 2.709	" 57	4.500 - 4.649
" 72	2.710 - 2.779	" 72	4.650 - 4.799
" 80	2.780 - 2.849	" 90	4.800 - 4.999
" 87	2.850 - 2.919		
" 94	2.920 - 2.999	Purple/10	5.000 - 5.199
		" 32	5.200 - 5.399
Black/ 02	3.000 - 3.059	" 50	5.400 - 5.599
" 10	3.060 - 3.139	" 71	5.600 - 5.799
" 17	3.140 - 3.209	" 92	5.800 - 5.999
" 24	3.210 - 3.279		
" 32	3.280 - 3.359	Yellow/60	6.000 - 6.299
" 40	3.360 - 3.430	Orange/65	6.300 - 6.699
" 48	3.440 - 3.519	Sand/68	6.700 - 6.999
" 56	3.520 - 3.599	Orange/70	7.000 - 7.399
" 64	3.600 - 3.679	" 76	7.400 - 7.899
" 72	3.680 - 3.759	" 80	7.900 - 8.499
" 80	3.760 - 3.839	" 90	8.500 - 9.499
" 88	3.840 - 3.919	" 99	9.500 -10.499
" 96	3.920 - 3.999		
Green/ 05	4.000 - 4.099	Sand/10	10.500 -11.999
" 15	4.100 - 4.199	White/20	12.0 & Greater

DECK B

Card No.	d/n Range	Card No.	d/n Range
Yellow/51	2.460 - 2.529	Green/ 10	4.050 - 4.149
" 54	2.530 - 2.599	" 20	4.150 - 4.249
" 62	2.600 - 2.669	" 30	4.250 - 2.349
" 69	2.670 - 2.739	" 40	4.350 - 4.449
" 75	2.740 - 2.809	" 50	4.450 - 4.569
" 85	2.810 - 2.879	" 65	4.570 - 4.719
" 92	2.880 - 2.949	" 80	4.720 - 4.899
" 99	2.950 - 3.019	" 99	4.900 - 5.099